Oxyfunctionalization of Aliphatic Esters by Methyl(trifluoromethyl)dioxirane

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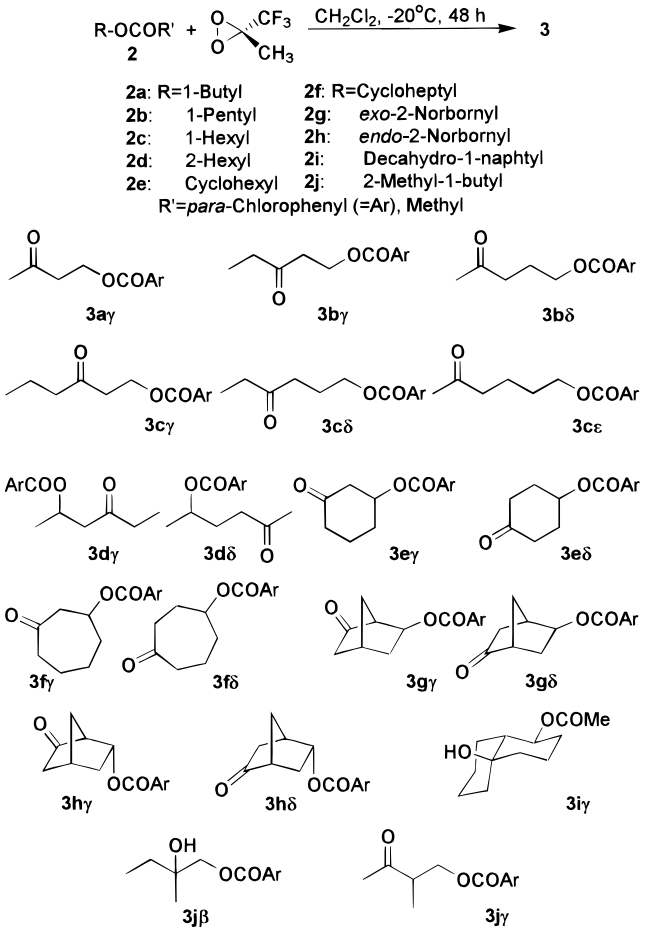
The oxidation of lineal, cyclic, and bicyclic aliphatic *p*-chlorobenzoic and *p*-chorobenzenesulfonic acid esters **2** with methyl(trifluoromethyl)dioxirane (TFDO) (**1**) occurs at positions in the hydrocarbon chain distant from the directing group with a significant degree of selectivity to give the corresponding keto or hydroxy esters. Compounds **2** are relatively deactivated with respect to this oxidation due to the electron-withdrawing nature of the ester moiety. Methylene C_α−H and C_β−H bonds remain unchanged in all cases, but tertiary C_β−H bonds undergo oxidation with TFDO (**1**). Stereoelectronic factors are used to explain the faster reaction rate in competition experiments for the oxidation of *endo*-norbornyl ester **2h** than for its *exo*-isomer **2g**.

Introduction

The selective oxyfunctionalization of hydrocarbons is a major topic in current organic synthesis.[1] Over the past few years, several chemical methods have been developed to achieve the oxidation of deactivated C−H bonds.[2] These include the oxidation of hydrocarbons with transition metals using, for example, metalloporphyrins,[3] ruthenium salts,[4] and peroxometalates.[5] Other methods are based on metal-free oxidants, such as ozone,[6] perfluoroalkyloxaziridines,[7] or dioxiranes.[8] These latter compounds, especially methyl(trifluoromethyl)dioxirane (**1**)[9] (TFDO), are outstanding reagents for the oxidation of C−H bonds of hydrocarbons due to their selectivity, mild reaction conditions, and chemical yield. In our continuing study of the factors that determine the selectivity of dioxiranes in the oxyfunctionalization of hydrocarbons, we report our results on the oxidation of lineal, cyclic, and bicyclic aliphatic esters with TFDO (**1**), which leads to the oxidation of distant positions in the hydrocarbon chain with a significant degree of selectivity.

Results and Discussion

Initially, the oxidation of *p*-chlorobenzoic acid esters **2** was carried out with ketone-free dichloromethane solutions of TFDO[10] at −20 °C (see the Experimental Section), to give readily isolable keto or hydroxy esters **3**. Reactions were monitored by iodometric titration[11] to control the consumption of TFDO (**1**). In general, the conversion



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(1) Arndtsen, B. A.; Bergan, R. G.; Mobley, T. A.; Peterson, T. H. *Acc. Chem. Res.* **1995**, *28*, 154.
(2) Reiser, O. *Angew. Chem.* **1994**, *106*, 73; *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 69.
(3) Meunier, B. *Chem. Rev.* **1992**, *92*, 1411.
(4) (a) Tenaglia, A.; Terranova, E.; Waegell, B. *Tetrahedron Lett.* **1989**, *30*, 5271. (b) Carlsen, H. J. *Synth. Commun.* **1987**, *17*, 19.
(5) Jaynes, B. S.; Hill, C. L. *J. Am. Chem. Soc.* **1995**, *117*, 4704.
(6) (a) Cohen, Z.; Keinan, E.; Mazur, Y.; Varkony, T. H. *J. Org. Chem.* **1975**, *40*, 2141. (b) Cohen, Z.; Keinan, E.; Mazur, Y.; Ulman, A. *J. Org. Chem.* **1976**, *41*, 2651. (c) Proksch, E.; de Meijere, A. *Angew. Chem.* **1976**, *88*, 802; *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 761. (d) Proksch, E.; de Meijere, A. *Tetrahedron Lett.* **1976**, 4851.
(7) (a) DesMarteu, D. D.; Donadelli, A.; Montanari, V.; Petrov, V. A.; Resnati, G. *J. Am. Chem. Soc.* **1993**, *115*, 4897. (b) Petrov, V. A.; DesMarteau, D. D. *J. Org. Chem.* **1993**, *58*, 4754.
(8) (a) Curci, R.; Dinoi, A.; Rubino, M. F. *Pure Appl. Chem.* **1995**, *67*, 811. (b) Adam, W; Hadjiarapoglou, L. P. *Topics in Current Chemistry*; Springer-Verlag: Berlin, 1993; Vol. 164, p 45. (c) Adam, W; Hadjiarapoglou; Curci, R.; Mello, R. *Organic Peroxides*; Wiley: New York, 1992; Chapter 4. (d) Curci, R. *Advances in Oxygenated Processes*; JAI: Greenwich, CT, 1990; Vol. 2, Chapter 1. (e) Murray, R. W. *Chem. Rev.* **1989**, *89*, 1187. (f) Adam, W.; Curci, R.; Edwards, J. O. *Acc. Chem. Res.* **1989**, *22*, 205.
(9) (a) Asensio, G.; Mello, R.; González-Núñez, M. E.; Castellano, G.; Corral, J. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 217. (b) Asensio, G.; González-Núñez, M. E.; Mello, R.; Boix-Bernardini, C.; Adam, W. *J. Am. Chem. Soc.* **1993**, *115*, 7250. (c) Adam, W.; Asensio, G.; Curci, R.; González-Núñez, M. E.; Mello, R. *J. Org. Chem.* **1992**, *57*, 953. (d) Mello, R.; Cassidei, L.; Fiorentino, M.; Fusco, C.; Curci, R. *Tetrahedron Lett.* **1990**, *31*, 3067. (e) Mello, R.; Fiorentino, M.; Fusco, C.; Curci, R. *J. Am. Chem. Soc.* **1989**, *111*, 6749.
(10) Adam, A.; Curci, R.; González-Núñez, M. E.; Mello, R. *J. Am. Chem. Soc.* **1991**, *113*, 7654.
(11) Adam, W.; Asensio, G.; Curci, R.; González-Núñez, M. E.; Mello, R. *J. Am. Chem. Soc.* **1992**, *114*, 8345.

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Table 1. Oxidation of Esters 2 with TFDO (1)[a]

		product distribution **3a**−**j**[c] (%)[c]			
entry	**2**[b]	β	γ	δ	ϵ
1	**a**		>98		
2	**b**		12[d]	88 (80)	
3	**c**		14[d]	29 (25)	57 (55)
4	**d**		8[d]	92 (90)	
5	**e**		40[d]	60 (56)	
6	**f**		15 (9)	85 (83)	
7	**g**		2[e]	98 (95)	
8	**h**		9 (5)	91 (90)	
9	**i**[f]		>98 (97)		
10	**j**	70 (68)	30 (25)		

[a] Reactions were carried out at −20 °C in CH_2Cl_2 for 48 h with an initial molar ratio **2**:**1** = 3. [b] Substrate conversion was 100% in all the cases. [c] From GC or NMR analysis of the crude reaction mixture; isolated yields are in parentheses. [d] Decomposes in the isolation process. [e] Not isolated. [f] Used as acetate.

of dioxirane was complete after 48 h. Compounds **3** were isolated by column chromatography and analyzed by GC, GC−MS, and ^{1}H- and ^{13}C-NMR. The results are shown in Table 1. Oxidations were also carried out with acetic, trifluoroacetic, and *p*-toluensulfonic acid esters without noticeable changes in selectivity. Slower oxidation rates were found for trifluoroacetic and *p*-chlorobenzenesulfonic acid esters, as expected from the stronger electron-withdrawing ability of the ester moiety in these cases. We should note that the aromatic rings of *p*-chlorobenzoic and *p*-chorobenzenesulfonic acid esters were stable in all cases against oxidation by **1**, although the reaction times were longer and the temperatures were higher than in other TFDO oxidations.

It is widely accepted that the oxidation of C−H bonds by TFDO (**1**) is an electrophilic process.[8] Consequently, compounds **2** are relatively deactivated with regard to this oxidation due to the electron-withdrawing nature of the ester moiety. The reactivity of the methylene groups in **2** increases with the distance to the ester function, as expected from the inductive nature of the directing effect. The observed product distribution reflects that the effect of the ester group is weakened with the distance along the aliphatic chain. Oxidation occurs preferentially at distant positions in the chain. Methylene C_α−H and C_β−H bonds remain unchanged in all cases (Table 1). In contrast, the tertiary C_β−H bond in compound **2j** is oxidized by TFDO (**1**) due to the preference shown by TFDO for the oxidation of tertiary hydrogens, which is well documented in simple hydrocarbons.[8,9e] Under the influence of the ester group, the reactivities of tertiary H_β and secondary H_γ hydrogens are similar, and consequently, the oxidation of compound **2j** gives a mixture of the hydroxy ester **3j**β and the keto ester **3j**γ (Table 1, entry 10). When two tertiary C−H bonds are present, as in compound **2i**, the oxidation is selective and occurs at the less-deactivated hydrogen position to exclusively give the hydroxy ester **3i**γ. Methyl groups are not oxidized in any case due to their low reactivity.[8,9e] β-Keto esters **3b**γ, **3c**γ, **3d**γ, and **3e**γ were identified in the crude reaction mixture by GC−MS and ^{1}H- and ^{13}C-NMR (Table 1). However, attempts to isolate these compounds by column chromatography were unsuccessful, probably due to the loss of carboxylic acid and subsequent polymerization of the resulting α,β-unsaturated carbonyl compound under our experimental conditions. A similar β-elimination process occurs in these keto esters when the crude reaction mixture is allowed to stand at room temperature for 24 h.

Methylene groups are converted directly into ketones by TFDO. However, it has been shown[9a,e] that this reaction occurs in two steps through the corresponding secondary alcohol, which undergoes further oxidation at C_α−H faster than any other C−H bond can react. In fact, we recently showed that the monohydroxylation of hydrocarbons[9a] can be achieved with TFDO in excellent yields when the oxidation is performed in the presence of an excess of trifluoroacetic anhydride to trap the hydroxy group as trifluoroacetic acid monoester, which does not to undergo further oxidation in the presence of unreacted hydrocarbon. On the other hand, in the reaction of norbornane with TFDO, *exo*-C−H bonds are hydroxylated much faster than their *endo* counterparts.[9a,e] To determine the relationship between oxidation rate, selectivity, and efficacy in the transmission of the electron-withdrawing effect from the ester moiety along C−C and C−H bonds, we carried out the competitive oxidation of an equimolar mixture of *exo*- and *endo*-norbonyl *p*-chlorobenzoates **2g** and **2h** with TFDO (**1**) in a molar ratio of 1:1:2 in dichloromethane at −20 °C. Under these conditions, we found that $k_{endo}/k_{exo} = 1.6 \pm 0.05$, which indicates that the C(6)− and C(5)−H_{exo} bonds of the *exo*-ester **2g** are more deactivated with respect to electrophilic attack by TFDO than the corresponding C(6)− and C(5)−H_{exo} bonds in the *endo*-ester **2h**. This suggests that there is a different level of deactivating hyperconjugative interaction between the ester moiety and the C−H_{exo} bonds in compounds **2g** and **2h**, most likely due to the different (*exo* or *endo*) orientation of the ester in each diastereomer. Since the hyperconjugative interaction[12] is transmitted by overlap of σ bonding orbitals of the cyclic framework with the antibonding σ^* orbital of the C(2)−O bond, the orbital interaction will be greater in the *exo*-ester **2g** than in the *endo*-isomer **2h**. This is consistent with the faster reaction rate observed for the oxidation of the *endo*-ester **2h** than for **2g** in the competition experiment. However, this effect is not accompanied by any significant increase in the regioselectivity in the oxidation (Table 1, entries 7 and 8). Notably, we found comparable regioselectivities in the oxidation of trifluoroacetic and arenesulfonic acid esters regardless of the stronger electron-withdrawing character of the ester group in these cases.

Conclusions

These results suggest that esterification is an efficient method for protecting primary and secondary aliphatic alcohols against oxidation by methyl(trifluoromethyl)-dioxirane (**1**) in the presence of hydrocarbons. While aliphatic esters are oxidized by **1**, oxidation occurs more slowly than with hydrocarbons due to the electron-withdrawing nature of the ester group. This oxidation occurs regioselectively at positions in the chain distant from the directing group. In this way, esters **2** are regioselectively converted into the corresponding keto esters or hydroxy esters **3** in good yields.

Experimental Section

General Aspects. GLC analyses were performed on a DB-1 capillary column (25 m, film thickness 1 μm, i.d. 0.25 mm), and GC−MS measurements were made on a PBX-5 capillary column (30 m, film thickness 1 μm, i.d. 0.23 mm).

(12) Lowry T. H.; Richardson, K. S. *Mechanism and Theory in Organic Chemistry*; HarperCollins Publishers: New York, 1987.

All solvents were purified by standard procedures and freshly distilled prior to use. Methyl(trifluoromethyl)dioxirane (**1**) in trifluoroacetone and ketone-free solutions of **1** in methylene chloride were obtained as reported[9e,10] starting from caroate and trifluoroacetone at pH *ca.* 7.5.

Oxidation of Alkyl *p*-Chlorobenzoates (2). General Procedure. To a stirred solution of cyclohexyl *p*-chlorobenzoate (**2e**) (0.29 mmol, 70 mg) in dichloromethane at −20 °C was added a 0.4 M dichloromethane solution of TFDO (initial molar ratio 1:3) in one batch, and the mixture was allowed to stand at −20 °C for 48 h. The reaction mixture was analyzed by GC and GC−MS. The volatiles were removed under vacuum at 0 °C, and the residue was dissolved in $CDCl_3$ and analyzed by NMR. Column chromatography (silica gel, *n*-hexane:dichloromethane 1:1) of the crude yielded 41.1 mg of 4-[(*p*-chlorobenzoyl)oxy]cyclohexanone (**3e**δ) (56%). The minor product 3-[(*p*-chlorobenzoyl)oxy]cyclohexanone (**3e**γ) decomposed during elution.

4-[(*p*-Chlorobenzoyl)oxy]-2-butanone (3aγ). ^{1}H NMR ($CDCl_3$, 250 MHz): δ 2.18 (s, 3H), 2.86 (t, J = 6.2 Hz, 2H), 4.53 (t, J = 6.2 Hz, 2H), 7.34 (d, J = 8.6 Hz, 2H), 7.88 (d, J = 8.6 Hz, 2H). ^{13}C NMR ($CDCl_3$, 62.8 MHz): δ 30.6, 42.2, 59.9, 128.2, 128.7, 130.9, 130.9, 139.5, 165.9, 205.9. MS (EI, 70 eV): *m*/*z* 228 (3.7), 226 (11.5), 158 (39.3), 156 (100), 141 (59.4), 139 (36.8), 111 (50.5), 75 (27.4). Exact mass: calcd for $C_{11}H_{11}ClO_3$ 226.0397, found 226.0391.

5-[(*p*-Chlorobenzoyl)oxy]-2-pentanone (3bδ). ^{1}H NMR ($CDCl_3$, 250 MHz): δ 2.00 (m, 2H), 2.12 (s, 3H), 2.55 (t, J = 7.2 Hz, 2H), 4.27 (t, J = 6.4 Hz, 2H), 7.36 (d, J = 8.6 Hz, 2H), 7.90 (d, J = 7.6 Hz, 2H). ^{13}C NMR ($CDCl_3$, 62.8 MHz): δ 22.8, 30.0, 39.9, 64.4, 128.6, 128.7, 130.9, 139.4, 165.7, 207.5. MS (EI, 70 eV): *m*/*z* 242 (0.3), 240 (0.5), 183 (31.0), 158 (30.6), 141 (100), 140 (30.7), 139 (65.9), 113 (30.0), 111 (81.7), 101 (89.3), 84 (96.7), 75 (38.1). Exact mass: calcd for $C_{12}H_{13}ClO_3$ 240.0553, found 240.0541.

6-[(*p*-Chlorobenzoyl)oxy]-3-hexanone (3cδ). ^{1}H NMR ($CDCl_3$, 250 MHz): δ 0.99 (t, J = 7.3 Hz, 3H), 2.00 (m, 2H), 2.38 (q, J = 7.3 Hz, 2H), 2.50 (t, J = 7.3 Hz, 2H), 4.25 (t, J = 6.4 Hz, 2H), 7.34 (d, J = 8.6 Hz, 2H), 7.89 (d, J = 8.6 Hz, 2H). ^{13}C NMR ($CDCl_3$, 62.8 MHz): δ 7.8, 22.8, 36.1, 38.5, 53.4, 64.5, 128.6, 128.7, 130.9, 139.4, 165.7, 210.3. MS (EI, 70 eV): *m*/*z* 158 (11.8), 157 (19.7), 156 (35.5), 141 (50.5), 139 (100), 111 (42.9), 98 (33.2). Exact mass: calcd for $C_{13}H_{16}ClO_3$ 255.0788, found 255.0783.

6-[(*p*-Chlorobenzoyl)oxy]-2-hexanone (3cϵ). ^{1}H NMR ($CDCl_3$, 250 MHz): δ 1.75 (m, 4H), 2.16 (s, 3H), 2.52 (t, J = 6.7 Hz, 2H), 4.32 (t, J = 6.0 Hz, 2H), 7.41 (d, J = 8.6 Hz, 2H), 7.97 (d, J = 8.6 Hz, 2H). ^{13}C NMR ($CDCl_3$, 62.8 MHz): δ 20.1, 28.1, 29.9, 42.9, 64.8, 128.7, 130.9, 139.3, 165.7, 208.4. MS (EI, 70 eV): *m*/*z* 158 (17.1), 157 (27.1), 156 (49.5), 141 (74.8), 141 (52.3), 111 (57.8), 98 (100), 75 (27.9). Exact mass: calcd for $C_{13}H_{16}ClO_3$ 255.0788, found 255.0782.

5-[(*p*-Chlorobenzoyl)oxy]-2-hexanone (3dδ). ^{1}H NMR ($CDCl_3$, 250 MHz): δ 1.36 (d, J = 6.2 Hz, 3H), 1.97 (q, J = 7.1 Hz, 2H), 2.14 (s, 3H), 2.54 (t, J = 7.4 Hz, 2H), 5.16 (m, J = 6.3 Hz, 1H), 7.39 (d, J = 8.6 Hz, 2H), 7.95 (d, J = 8.6 Hz, 2H). ^{13}C NMR ($CDCl_3$, 62.8 MHz): δ 20.1, 29.7, 30.0, 39.5, 71.2, 128.6, 128.8, 130.9, 139.3, 165.2, 207.7. MS (EI, 70 eV): *m*/*z* 157 (5.3), 156 (5.4), 141 (32.3), 139 (100), 115 (31.0), 98 (26.4). Exact mass: calcd for $C_{13}H_{16}ClO_3$ 255.0788, found 255.0784.

4-[(*p*-Chlorobenzoyl)oxy]cyclohexanone (3eδ). ^{1}H NMR ($CDCl_3$, 250 MHz): δ 2.06 (m, 4H), 2.48 (m, 2H), 2.60 (m, 2H), 5.42 (m, 1H), 7.45 (d, J = 8.6 Hz, 2H), 8.00 (d, J = 8.5 Hz, 2H). ^{13}C NMR ($CDCl_3$, 62.8 MHz): δ 30.5, 37.3, 69.4, 128.8, 130.9, 139.7, 164.9, 209.7. MS (EI, 70 eV): *m*/*z* 156 (4.0), 141 (33.8), 139 (100.0), 111 (25.0), 96 (57.9). Exact mass: calcd for $C_{13}H_{14}ClO_3$ 253.0631, found 253.0640.

3-[(*p*-Chlorobenzoyl)oxy]cycloheptanone (3fγ). ^{1}H NMR ($CDCl_3$, 250 MHz): δ 2.00 (m, 6H), 2.58 (m, 2H), 2.94 (m, 2H), 5.40 (m, 1H), 7.41 (d, J = 8.5 Hz, 2H), 7.93 (d, J = 8.6 Hz, 2H). ^{13}C NMR ($CDCl_3$, 62.8 MHz): δ 23.8, 24.8, 35.1, 44.4, 48.3, 70.1, 128.5, 128.7, 130.9, 139.6, 164.6, 210.2. MS (EI, 70 eV): *m*/*z* 266 (0.4), 141 (33.5), 139 (100.0). Exact mass: calcd for $C_{14}H_{15}ClO_3$ 266.0710, found 266.0701.

4-[(*p*-Chlorobenzoyl)oxy]cycloheptanone (3fδ). ^{1}H NMR ($CDCl_3$, 250 MHz): δ 2.06 (m, 6H), 2.65 (m, 4H), 5.28 (m, 1H), 7.42 (d, J = 8.6 Hz, 2H), 7.96 (d, J = 8.6 Hz, 2H. ^{13}C NMR ($CDCl_3$, 62.8 MHz): δ 19.0, 28.7, 34.8, 37.7, 43.4, 73.8, 128.7, 130.9, 139.5, 164.7, 213.3. MS (EI, 70 eV): *m*/*z* 266 (0.2), 141 (42.0), 139 (100.0), 111 (53.3). Exact mass: calcd for $C_{14}H_{15}ClO_3$ 266.0710, found 266.0709.

***exo*-2-[(*p*-Chlorobenzoyl)oxy]norbornan-6-one (3gγ).** ^{1}H NMR ($CDCl_3$, 250 MHz): δ 1.84 (m, 3H), 2.07 (m, 3H), 2.84 (m, 2H), 5.06 (m, 1H), 7.35 (d, J = 8.4 Hz, 2H), 7.88 (d, J = 8.7 Hz, 2H). ^{13}C NMR ($CDCl_3$, 62.8 MHz): δ 3.0, 36.1, 38.7, 44.7, 56.8, 72.7, 128.4, 128.7, 130.3, 139.6, 164.8, 219.4. MS (EI, 70 eV): *m*/*z* 238 (13. 3), 236 (41.0), 141 (28.4), 138 (100.0). Exact mass: calcd for $C_{14}H_{13}ClO_3$ 264.0553, found 264.0548.

***exo*-2-[(*p*-Chlorobenzoyl)oxy]norbornan-5-one (3gδ).** ^{1}H NMR ($CDCl_3$, 250 MHz): δ 1.97 (m, 6H), 2.63 (d, J = 4.8 Hz, 1H), 2.84 (d, J = 4.8 Hz, 1H), 5.05 (d, J = 6.8 Hz, 1H), 7.39 (d, J = 8.6 Hz, 2H), 7.92 (d, J = 8.6 Hz, 2H). ^{13}C NMR ($CDCl_3$, 62.8 MHz): δ 33.4, 34.4, 39.8, 40.7, 48.7, 75.6, 128.4, 128.7, 130.9, 139.5, 165.1, 215.0. MS (EI, 70 eV): *m*/*z* 266 (1.2), 264 (3.7), 139 (100.0), 108 (26.4). Exact mass: calcd for $C_{14}H_{13}ClO_3$ 264.0553, found 264.0559.

***endo*-2-[(*p*-Chlorobenzoyl)oxy]norbornan-6-one (3hγ).** The compound was identified by GC−MS in the crude reaction mixture. MS (EI, 70 eV): *m*/*z* 266 (0.7), 267 (1.6), 141 (33.5), 139 (100.0), 111(29.2). Exact mass: calcd for $C_{14}H_{13}ClO_3$ 264.0553, found 264.0545.

***endo*-2-[(*p*-Chlorobenzoyl)oxy]norbornan-5-one (3hδ).** ^{1}H NMR ($CDCl_3$, 250 MHz): δ 1.55 (m, 1H), 1.85 (m, 2H), 2.15 (m, 1H), 2.52 (m, 2H), 2.67 (m, 1H), 3.07 (m, 1H), 5.44 (m, 1H), 7.43 (d, J = 8.6 Hz, 2H), 7.95 (d, J = 8.6 Hz, 2H). ^{13}C NMR ($CDCl_3$, 62.8 MHz): δ 33.1, 36.1, 38.2, 39.3, 49.9, 73.9, 128.1, 128.8, 130.9, 139.7, 165.4, 215.9. MS (EI, 70 eV): *m*/*z* 266 (2.7), 264 (7.2), 141 (28.8), 139 (100.0). Exact mass: calcd for $C_{14}H_{13}ClO_3$ 264.0553, found 264.0553.

1-Acetoxy-*cis*-10-decalol (3iγ). ^{1}H NMR ($CDCl_3$, 250 MHz): δ 1.40 (m, 15H), 2.03 (s, 3H), 5.31 (m, 1H). ^{13}C NMR ($CDCl_3$, 62.8 MHz): δ 19.4, 21.3, 22.4, 23.7, 25.2, 25.3, 29.7, 41.8, 46.3, 53.4, 72.5, 73.5, 170.8. MS (EI, 70 eV): *m*/*z* 153 (14.8), 152 (89.5), 134 (56.1), 124 (66.7), 123 (37.1), 110 (46.8), 109 (38.0), 95 (35.7), 55 (40.9), 43 (100.0), 41 (32.9). Exact mass: calcd for $C_{12}H_{20}O_3Na$ (M^+ + Na) 235.1310, found 235.1312.

1-[(*p*-Chlorobenzoyl)oxy]-2-methyl-2-butanol (3jβ). ^{1}H NMR ($CDCl_3$, 250 MHz): δ 0.98 (t, J = 7.5 Hz, 3H), 1.27 (s, 3H), 1.66 (q, J = 7.6 Hz, 2H), 4.22 (s, 2H), 7.44 (d, J = 8.7 Hz, 2H), 7.98 (d, J = 8.6 Hz, 2H). ^{13}C NMR ($CDCl_3$, 62.8 MHz): δ 7.9, 23.4, 31.7, 71.3, 72.1, 128.3, 128.8, 131.0, 139.6, 165.7. MS (EI, 70 eV): *m*/*z* 213 (2.6), 139 (62.1), 73 (100.0. Exact mass: calcd for $C_{13}H_{16}ClO_3$ 255.0788, found 255.0785.

4-[(*p*-Chlorobenzoyl)oxy]-3-methyl-2-butanone (3jγ). ^{1}H NMR ($CDCl_3$, 250 MHz): δ 1.23 (d, J = 7.2 Hz, 3H), 2.25 (s, 3H), 3.02 (m, J = 7.1 Hz, 1H), 4.44 (m, 2H), 7.40 (d, J = 8.6 Hz, 2H), 7.93 (d, J = 8.6 Hz, 2H). ^{13}C NMR ($CDCl_3$, 62.8 MHz): δ 13.4, 28.7, 46.0, 65.9, 128.2, 128.8, 130.9, 165.4, 209.3. MS (EI, 70 eV): *m*/*z* 199 (11.3), 156 (38.2), 141 (35.7), 139 (100.0), 111 (25.7), 43 (82.5). Exact mass: calcd for $C_{13}H_{16}ClO_3$ 255.0788, found 255.0780.

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Supporting Information Available: ^{1}H and ^{13}C NMR spectra of compounds **3a**γ, **3b**δ, **3c**δ, **3c**ϵ, **3d**δ, **3e**δ, **3f**γ, **3f**δ, **3g**γ, **3g**δ, **3h**δ, **3i**γ, **3j**β, and **3j**γ (28 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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